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## HIGH YIELD SYNTHESIS OF DIAMINO-SUBSTITUTED SILSESQUOXANE BUILDING BLOCKS

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Polyhedral oligomeric silsesquioxane (POSS) materials are monodisperse oligomers of  $(\text{RSiO}_{1.5})_n$  that have found application as property enhancers in many thermoset and thermoplastic systems. However, there are not many high-yield scaleable syntheses available for producing POSS diamines suitable for incorporation into high-temperature materials. High-yield scalable syntheses were designed and implemented to produce a family of phenylPOSS derivatives containing two aniline groups. These amino functionalities can be either *meta*, *meta*- or *para*, *para*- on the aromatic groups. The POSS groups can be either pendent to the amino groups or else "in chain". When these POSS are mixed with other diamines similar to ODA they are easily copolymerized with dianhydrides from the PMDA family to make a variety of polyimides. Exploration of the properties of such polyimides and oligoimides is underway with the goal to delineate the effect of the stereochemistry of the POSS on the properties of the polymer.

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## Introduction

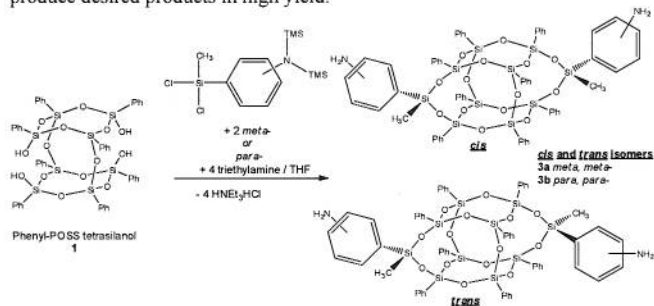
Polyhedral oligomeric silsesquioxane (POSS) materials are monodisperse oligomers of  $(\text{RSiO}_{1.5})_n$  (the octamer with  $n = 8$  is the most common) that have found application as property enhancers in many thermoset and thermoplastic systems.<sup>1</sup> The inorganic  $\text{SiO}_{1.5}$  core can impart a thermoxidative resistance to a polymer while the R-groups play a major role in the compatibility of the POSS with the polymer matrix. POSS with amine functionality have found application as reactants in both epoxy and polyimide systems.<sup>2</sup> However, there are not many scalable syntheses available for producing POSS diamines in high yield. In addition, most synthetic schemes to diaminoPOSS result in materials containing alkyl groups which result in a lower degree of desired thermal stability.

## Experimental

Phenyl-POSS tetrasilanol, **1** and phenyl-POSS trisilanol **2**, were obtained from Hybrid Plastics and used as received.  $\text{SiCl}_4$  and  $\text{MeSiCl}_3$  were obtained from United Chemical Technologies, distilled and stored under nitrogen prior to use. Anhydrous solvents were further dried by passage thru an activated alumina column under a nitrogen atmosphere. 3-[Bis(trimethylsilyl)amino]phenylmagnesium chloride solution in THF (Aldrich), 4-Bromo-*N,N*-bis(trimethylsilyl)aniline (Aldrich), and Magnesium (Aldrich), were used as received. Oxydianiline, 4, 4'-Diaminodiphenyl ether, ODA, (Lancaster Synthesis) was recrystallized from DMF/toluene. Pyromellitic dianhydride, PMDA, (Aldrich) was recrystallized from dioxane. Triethylamine (Aldrich) was dried by distillation from  $\text{CaH}_2$  and stored under nitrogen prior to use. In general, all manipulations were carried out under a dry nitrogen atmosphere in a Vacuum Atmosphere dry box or by using standard Schlenk line techniques. NMR spectra were obtained on either a 300 or 400 MHz Bruker spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  spectra are referenced to internal solvent; residual  $\text{CHCl}_3$  at 7.26 ppm for proton, and  $\text{CDCl}_3$  at 77.00 ppm for carbon.  $^{29}\text{Si}$  spectra are referenced to external  $\text{SiMe}_4$  in  $\text{CDCl}_3$  at 0 ppm, and obtained using an inverse gated  $30^\circ$  pulse with a 12 – 20 second delay between pulses. The detailed syntheses of all materials are contained in recent publications.<sup>3,4</sup>

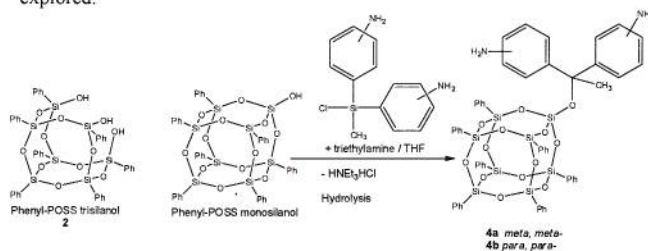
## Results and Discussion

The goal of this work was to produce a high-yield, reproducible set of scalable syntheses to POSS diamines which have a maximum possible thermal stability. Two POSS starting materials were used to achieve these ends: a phenyl-POSS tetrasilanol, **1**, and a phenyl-POSS trisilanol, **2**, (See figures 1 & 2). Both of these commercially available POSS silanols react readily with appropriately substituted chlorosilanes in the presence of triethylamine to produce desired products in high yield.

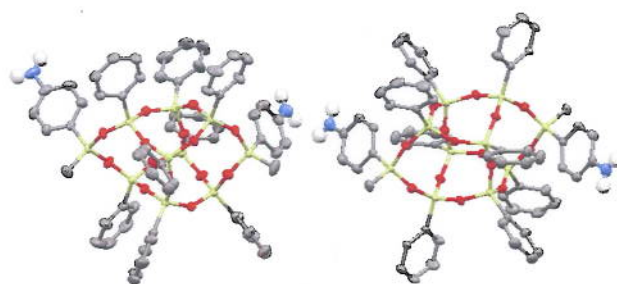


**Figure 1.** Synthesis of “in-chain” diaminoPOSS. Both *meta*, *meta*- and *para*, *para*- derivatives were produced; each of these also make a 50:50 mixture of *cis* and *trans* isomers.

Chlorosilanes were synthesized that could be used to produce POSS-disilanol containing aromatic or siloxy linkages to maximize thermal stability. Also desired were POSS diamines that had the POSS unit either pendent to the diamine linkage or else with an “in-chain” architecture. These two types of building blocks allow for the production of a series of thermoplastic diaminoPOSS copolymers where the effect of POSS architecture can be fully explored.



**Figure 2.** Synthesis of “pendent” diaminoPOSS. Both *meta*, *meta*- and *para*, *para*- derivatives were produced



**Figure 3.** X-ray crystal structures of both *cis*-**3b** (left) and *trans*-**3b** (right). Only shown are the cores of the structures. Silicon atoms are yellow, oxygen atoms are red, carbon atoms are gray and nitrogen atoms are blue.

## Conclusions

High yield scalable syntheses were designed and implemented to produce phenylPOSS derivatives containing two aniline groups. These amino functionalities can be either *meta*, *meta*- or *para*, *para*- on the aromatic groups. The POSS groups can be either pendent to the amino groups or else “in chain”. In addition, the “in chain” derivatives produce equal amounts of *cis*- and *trans*-isomers which can be separated by fractional crystallization. The absolute stereochemistry of these two isomers was determined by single crystal X-ray crystallography. When these POSS are mixed with other diamines similar to ODA they are easily copolymerized with dianhydrides from the PMDA family to make a variety of polyimides. Exploration of the properties of such polyimides and oligoimides is underway with the goal to delineate the effect of the stereochemistry of the POSS on the properties of the polymer.

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## References.

- (1) Cordes, D. B.; Lickiss, P. D.; Ratabouol, F. *Chem. Rev.*, **2010**, *110* (4), 2081-2173.
- (2) Kuo, S-W.; Huang, C-F.; Chang, F-C. *Recent Advances in Polymer Nanocomposites: Synthesis and Characterisation* (2010), 155-190.
- (3) Seurer, B.; Haddad, T.; Mabry, J.M.; Lee, A. *Macromolecules*. **2010**, *43*, 9337 - 9347
- (4) Vij, V., Yandek, G., Ramirez, S., Mabry, J., Haddad, T. *Silicon*, Submitted for publication.